

# EFFECT OF ELECTROREDUCTION PRETREATMENT IN AQUEOUS MEDIA ON HYDROPYROLYSIS OF A BITUMINOUS COAL

Li Baoqing

Service de Chimie Générale et Carbochimie, Université Libre de  
Bruxelles, Av. F.D. Roosevelt, 50(CP 165), B-1050, Bruxelles, Belgium

Keywords: electrochemical reduction, hydropyrolysis, pretreatment

## Abstract

Electroreduction of coal (ER) is studied in aqueous tetrabutylammonium hydroxide (TBAOH) solution and tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>)-THF-H<sub>2</sub>O solution by using platinum as anode and Hg pool as cathode. The electrolysis in aqueous TBAOH solution seems to have little effect on the following hydropyrolysis (HyPy) although the pyridine extractable yield of the reduced coal increases. In an undivided cell the re-oxidation of the reduced coal occurs. Cathodic reduction in TBABF<sub>4</sub>-THF-H<sub>2</sub>O solution gives a pronounced effect on HyPy. Higher conversion (60.9%) and total oil yield (50.6%) (THF soluble + oil formed in HyPy) are obtained in a divided cell as compared with 42.1% and 28.4% for untreated coal, respectively. The electroreduction pretreatment of coal enhances the rate of oil formation and oil yield in HyPy, indicating that the reduced coal can be depolymerized more easily due to the solvolysis and hydrogenation.

## Introduction

The conversion of coal to oil needs undoubtedly to increase the H/C ratio in coal. Therefore, gaseous hydrogen is always used in coal liquefaction, HyPy and other hydrogenation processes. Considering the high activation energy for the dissociation of gaseous hydrogen, the addition of hydrogen to coal using gaseous hydrogen is so difficult that the elevated pressure has to be used. As a result, the high cost makes these processes hardly competitive with those using petroleum as raw materials. To reduce the hydrogen consumption and even to avoid the use of gaseous hydrogen and/or elevated pressure are very interesting in coal hydrogenation processes.

Previous studies<sup>1-3</sup> showed the possibility to improve the quantity and quality of oil and the efficiency of hydrogen utilization in HyPy by pretreatment of coal using catalyst and various gases. Although these pretreatments are effective, the improvements are still not optimistic even the use of impregnated sulphided Mo catalyst because of the cost of catalyst and an increasing sulphur content in char.

Earlier studies<sup>4,5</sup> indicated that hydrogen can be added to coal by electroreduction using LiCl as electrolyte in an organic solvent. Recently, It is reported<sup>6</sup> that hydrogenation of coal can be carried out by electroreduction in an aqueous solution. They used a mediator (CrCl<sub>3</sub>)/Ni powder/LiCl/aqueous THF solution/ultrasonic irradiation system, which is too complicated to be performed practically. It is known<sup>7-9</sup> that the effective electroreduction of benzene and related compounds can be performed in tetraalkylammonium aqueous solution. Reduction in water is economically attractive because of the cost and of the high conductivity of the medium. Kariv-Miller<sup>7</sup> has mentioned that a practical application of this method could be in hydrogenation processes which are important for coal conversion. However, the studies are still limited to the model compounds.

This research is aimed to investigate the cathodic reduction of coal in aqueous solution using TBAOH and TBABF<sub>4</sub> as electrolyte. The effects of various parameters on electroreduction of coal are studied in TBAOH solution system, while the cathodic reduction in TBABF<sub>4</sub>-THF-H<sub>2</sub>O solution is investigated as comparison.

### Experimental

A cylindrical cell, 15 cm high, with a hot water jacket and a 44,18 cm<sup>2</sup> mercury pool cathode at the bottom is used as a electrolysis cell. With a fritted glass-cup dipped in the solution as an anode compartment it is a divided cell. A coiled platinum wire is used as anode (7,85 cm<sup>2</sup>). The reference electrode is a calomel electrode. The cell is fitted a thermometer, a gas exit with a reflux condenser and a gas inlet for a nitrogen flow during the electrolysis. The cell is filled with 45 ml Hg, 150 ml electrolyte solution and 7,5 g coal (as received). The stirring is carried out during electrolysis by means of a magnetic bar placed on the mercury surface.

Mercury is purified before use. All the electrolyses are performed by using constant current. During electrolysis the cathode potential and the cell voltage are recorded. Gas formed during electrolysis is totally collected in a tyre. Hydrogen in gas is analysed by G.C. and oxygen in gas is determined by paramagnetic Magnos 3 analyser.

After electrolysis mercury is separated and the treated coal is filtered out. When TBAOH is used as electrolyte, the treated coal is washed with water, 10% HCl and again with water to neutral state. In the case of as electrolyte, the treated coal is washed by THF, dried and then extracted with THF in a Soxhlet for 6 hr. The washed coal is dried at reduced pressure for one night. Although more or less grey 'TBA-Hg' compound which is difficult to be separated from the reduced coal, it can be evaporated and/or decomposed before 600 K, i.e. before coal thermal decomposition occurs. Thus, the content of 'TBA-Hg' in the reduced coal can be estimated by thermogravimetric study.

The effect of electroreduction pretreatment on HyPy is studied in a thermobalance under 3 MPa and heating rate of 5 K/min upto 1073 K. The oil yield is determined by carbon balance. Pyridine extraction is carried out in a Soxhlet with a sample of 1 g under nitrogen for 24 hr. The residue is dried at 60 °C and reduced pressure for 6 hr.

A bituminous Beringen Belgian coal with a granulometry of 45-90 µm is used in this study. Its characteristics are: proximate analysis (wt%, as received): moisture, 1.5; ash, 4.7; volatile matter, 34.5; ultimate analysis (wt%, daf): C, 84.7; H, 4.9; N, 1.7; S, 0.9; O (by difference), 7.8.

### Results and Discussion

#### 1. Electroreduction in TBAOH Aqueous Solution

The effects of various parameters on pyridine extractable yield, current efficiency for H<sub>2</sub> production and oil yield in HyPy of the reduced coal are listed in Table 1.

The electrolyte concentration remarkably influences the electro-chemical reactions. When TBAOH concentration decreases from 40% to 30%,

pyridine extractable yield is reduced from 17.0% to 7.6%. With increasing concentration, the current efficiency for hydrogen production decreases from 68.7% with 30% TBAOH solution to 46.6% with 55% TBAOH solution.

The influence of current density ranging from 1 to 8 A/dm<sup>2</sup> is shown in Table 1. The higher pyridine extractable yield is given with a current density of 4 A/dm<sup>2</sup> in a 40% TBAOH solution. Similar results were obtained by other authors in the study on effect of current density on current efficiency in electroreduction of benzene in TBAOH solution<sup>7</sup>.

It is suggested that the first step for the electroreduction in TBAOH solution is the formation of TBA-metal which could transfer an electron to the aromatic hydrocarbon to initiate the reduction<sup>7,11</sup>. The formation of colloidal Hg on the cathode surface is visually apparent during electrolysis. The slow formation of the colloidal Hg might be related to the current density and time.

It is also found that CO<sub>2</sub> yield obtained in HyPy enhances with increasing current densities. Re-oxidation of the reduced coal appears to occur, which will be discussed later.

Figures 1 and 2 show the influence of current density on conversion and oil yield formed in HyPy of the electroreduced coal. About 4% higher conversion and 3% more oil yield are obtained from the coal reduced in a 55% TBAOH solution than from the unreduced coal.

With increasing charge the current efficiency for H<sub>2</sub> production increases, while the pyridine extractables decreases at 0.088 F/g(daf) of charge transferred.

Table 2 shows the comparison of elemental analysis between raw coal and reduced coal. After electrolysis the H/C atomic ratio slightly increases from 0.69 to 0.70, while the O/C ratio enhances from 0.07 to 0.10. 1 hydrogen and 3 oxygen atoms per 100 carbon atoms are added to coal after electrolysis in these conditions, indicating the re-oxidation of cathodic reduced coal in an undivided cell.

Table 1 also compares the results obtained by electrolysis of coal at 60 °C and 80 °C using a 55 % TBAOH solution in an undivided cell. An increase in temperature decreases the current efficiency for the production of hydrogen. The little higher pyridine extractable yield and less current efficiency for hydrogen production obtained in a 40% TBAOH solution at 80°C also demonstrates the positive effect of the temperature on the reduction. However, the oil yields formed in HyPy of the coal reduced at 60 °C and 80 °C are the same.

The comparison of electrolysis in divided and undivided cell shows that lower pyridine extractable yield and higher current efficiency for hydrogen production are obtained in electrolysis with the divided cell. These might result from the re-oxidation in undivided cell as described before.

The comparison of elemental analysis of reduced coal in divided and undivided cells are also given in Table 2. The O/C ratio of the reduced coal in the divided cell is unchanged as compared to the raw coal, while it increases in the undivided cell. This further indicates the re-oxidation of the reduced coal in the undivided cell. The comparison of CO<sub>2</sub> yield (Figure 3) formed in HyPy of coal reduced in the same

conditions gives another prove. The higher CO<sub>2</sub> yield is produced in HyPy of the coal pretreated in the undivided cell.

The oil yield obtained in HyPy of the reduced coal in various conditions is 2-4% higher than that of the raw coal. The electrolysis in aqueous TBAOH solution seems to have little effect on the following HyPy although the pyridine extractable yield increase. Kariv-Miller et al.<sup>8</sup> concluded that the solubilization of the reactant in water by TBAOH could be an important factor. Coal can be easily dispersed but is hardly dissolved in a TBAOH solution (See Table 1). The less efficiency in improving the oil yield may be related to the low solubility of coal and its reduction products in TBAOH solution<sup>8</sup>. Therefore, the electro-reduction of coal in a TBAOH solution is not sensible to the various parameters and little or not efficient for subsequent HyPy.

## 2. Electroreduction in a TBABF<sub>4</sub>-THF-H<sub>2</sub>O Solution

Electroreduction of coal in 0.5 M TBABF<sub>4</sub>-THF-H<sub>2</sub>O(5 M) solution is performed at 33 °C, a current density of 0.6 A/dm<sup>2</sup> and a charge amount of 0.16 F in divided and undivided cells. The results are shown in Table 3. As a comparison, the results obtained in 55% TBAOH solution and catalytic HyPy using impregnated sulphided Mo catalyst are also listed.

The THF soluble yield for raw coal is 4.5%, indicating the solubility of coal in THF. After electrolysis in the divided cell the THF solubles markedly increase to 21.7%, showing the notable depolymerization of coal during electrolysis. The less THF solubles obtained in electrolysis in the undivided cell (12.4%) demonstrates that electro-reduction in the divided cell is much more effective than in the undivided cell. This may be due to the re-oxidation of reduced coal in the undivided cell as described in electrolysis in TBAOH solution.

The dramatic increase in THF solubles also indicates that the electron and proton produced in electrolysis can attack to not only the weak bonds but also macromolecular structure in coal, leading to the depolymerization of coal. The products thus formed can be dissolved in THF and be further reduced in solution. Due to the remove of the products by dissolution, more surface are exposed to electron and proton and thus, more THF solubles are produced. This may explain the importance of solubility of products.

The conversion and oil yield produced in HyPy of reduced coal are shown in Table 3 and Figures 4 and 5. Cathodic reduction in TBABF<sub>4</sub>-THF-H<sub>2</sub>O solution gives a pronounced effect on HyPy. Higher conversion (60.9%) and total oil yield (50.6%) are obtained in a divided cell as compared with 42.1% and 28.4% for unreduced coal respectively. The cathodic reduction of coal is found to be a better method for coal pretreatment even compared to catalytic HyPy using impregnated sulphided Mo catalyst (conversion: 47.7%; oil yield: 38.4%). That the conversion and oil yield for reduced coal in divided cell are much higher than in undivided cell also proves the extensive hydrogenation during electroreduction in divided cell. The conversion and oil yield in HyPy of the solvated coal are less than raw coal because some soluble substances which will be converted to oil are already removed during solution.

The elemental analysis of reduced coal is also shown in Table 2. Although the H/C ratio in the reduced coal is lower than that in raw coal, it is higher than in the solvated coal. The low value of H/C in

solvated coal indicates the THF solubles with high H/C value. Considered the THF solubles is much higher in electroreduced coal than in solvated coal, a considerable of hydrogen does add to electroreduced coal.

Figure 6 gives the rate of oil formation in HyPy. The reduced coal increases the rate of oil formation in HyPy. The enhances for the reduced coal in divided cell are higher than that in undivided cell. Like catalytic HyPy using impregnated sulphided Mo catalyst<sup>3</sup>, the remarkable increase in the rate of oil formation appears in the pyrolytic and hydrogenation stages (< 800 K), while the second peak (> 800 K) formed by hydrocracking reactions is disappeared. This indicates that the added hydrogen to coal in electroreduction enhances the amount of the intrinsic hydrogen which can saturate the free radicals at low temperature. When more free radicals are stabilized by hydrogenation, less polycondensation reactions take place and thereby less hydrocracking reactions occur at high temperatures, leading to the disappearance of the second peak in the rate of oil formation. The similar behaviours between catalyst-impregnated coal and electroreduced coal in HyPy show that hydrogenation reactions can be accelerated by using either catalyst or electrolysis. However, the functions of both processes are different. Electroreduction adds hydrogen into coal, while the promotion of hydrogenation by catalyst is related to the ability of adsorption and dissociation of gaseous hydrogen.

The problems for electrochemical reduction of coal in TBABF<sub>4</sub>-THF-H<sub>2</sub>O are the use of Hg and divided cell and the separation of TBABF<sub>4</sub> from THF solubles and reduced coal. However, electrochemical reduction of coal is an attractive method for pretreatment in hydrogenation processes of coal because of high conversion and oil yield and is worth investigating further for practical use.

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TABLE 1 EFFECT OF SOME PARAMETERS IN ELECTROREDUCTION OF COAL USING TBAOH SOLUTION ON PYRIDINE EXTRACTABLES, CURRENT EFFICIENCY FOR HYDROGEN AND OIL YIELD IN HyPy UNDER 3 MPa, 5 K/min, 913 K

Type	T °C	I A/dm <sup>2</sup>	Q F/g(daf)	TBAOH C. wt%	Ex.Yield wt%,daf	Effi.for H <sub>2</sub> %	Oil Yield wt%,daf
--	--	--	--	--	11,8	--	28.4
--	60	--	--	40	11,8	--	/
Undiv.	60	2	0.022	40	13,7	52,5	/
	60	4	0.022	40	17,0	52,9	29.3
	60	6	0.022	40	14,0	31,9	/
	60	4	0.022	30	7,6	68,7	/
	60	4	0.044	40	16,4	58,4	/
	60	4	0.088	40	4,2	69,9	/
	80	8	0.022	40	18,4	41,5	/
	60	4	0.022	55	N.D.*	46,6	31.2
	60	2	0.022	55	N.D.	27,8	32.6
	60	1	0.022	55	N.D.	27,3	33.8
	80	4	0.022	55	N.D.	27,2	32.3
Divided	60	4	0.022	40	14,9	52,9	29,9
	60	4	0.022	55	N.D.	68,4	31,3
	60	2	0.022	40	9,7	85,9	/

\* Not Determined. After electrolysis coal seems to be a mixture with TBAOH and mercury.

TABLE 2 ELEMENTAL ANALYSIS OF ELECTROREDUCED COAL

wt%, daf	Raw Coal	TBAOH*		TBABF <sub>4</sub> ^	
		Undiv. Cell	Divided Cell	Solcated Coal	ER-Coal
C	84.7	81.9	84.6	84.0	85.8
H	4.9	4.8	4.9	4.1	4.4
N	1.7	1.7	2.0	1.7	1.9
S	0.9	0.9	0.9	N.D.*	N.D.
O(by difference)	7.8	10.7	7.5	10.2*	7.9*
H/C	0.69	0.70	0.70	0.59	0.62
O/C	0.07	0.10	0.07	0.08	0.06

\* Electrolysis in 40% TBAOH, 60 °C, 4 A/dm<sup>2</sup>, 0.022 F/g(daf)

^ Electrolysis in TBABF<sub>4</sub> -THF-H<sub>2</sub>O, 0.6 A/dm<sup>2</sup>, 33°C, 0.022 F/g(daf), Divided Cell

\* Not Determined

• O+S: by difference

.. Assume 0.9% of sulphur content

TABLE 3 COMPARISON OF ELECTROREDUCTION PRETREATMENT AND CATALYTIC HyPy  
HyPy: 3 MPa, 5 K/min, 913 K

Type	THF Soluble (wt% daf)	Oil Yield in HyPy (wt% daf)		Total Oil Yield (wt% daf)	Conversion (wt% daf)	
		as Treated	as Raw Coal		as Treated Coal	as Raw Coal
Raw Coal		/	28.4	28.4	/	42.1
Electrolysis						
TBAF <sub>4</sub>						
Solvated	4.5	27.9	26.6	31.1	41.6	44.2
Undiv. Cell*	12.4	30.3	26.5	38.9	44.2	51.1
Divided Cell*	21.7	36.9	28.9	50.6	50.0	60.9
TBAOH <sup>^</sup>						
Undiv. Cell		/	31.2	30.1	/	43.3
Divided Cell		/	31.3	31.3	/	43.8
Catalytic HyPy*		/	38.4	38.4	/	47.7

\* 0.5 M TBABF<sub>4</sub> - THF-H<sub>2</sub>O (5 M), 0.6 A/dm<sup>2</sup>, 0.022 F/g(daf), 33 °C

<sup>^</sup> 55% TBAOH in H<sub>2</sub>O, 4 A/dm<sup>2</sup>, 0.022 F/g(daf), 60 °C

# Impregnated MoS<sub>2</sub> (0.5% Mo), 3 MPa, 5 K/min, 873 K

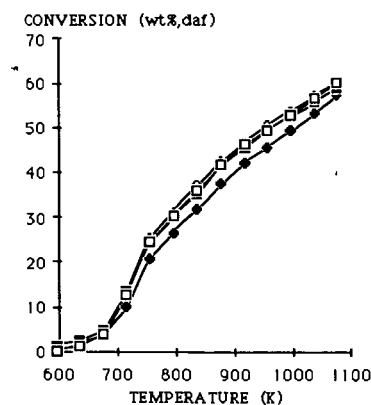


Fig. 1 Effect of Current Density in ER Pretreatment on Conversion in HyPy under 3 MPa, 5 K/min. ER: 40% TBAOH, 60 °C, 0.022 F/g(daf), Undiv. Cell.  
● Raw Coal; ○ 1 A/dm<sup>2</sup>; ■ 2 A/dm<sup>2</sup>; □ 4 A/dm<sup>2</sup>

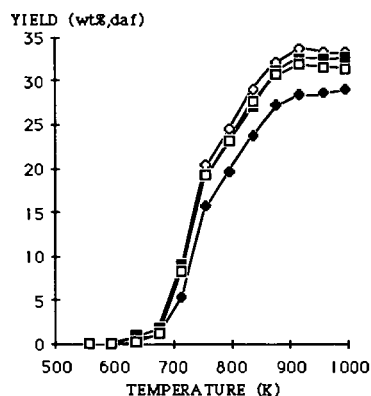


Fig. 2 Effect of Current Density in ER Pretreatment on Oil Yield in HyPy under 3 MPa, 5 K/min. ER: 40% TBAOH, 60 °C, 0.022 F/g(daf), Undiv. Cell.  
● Raw Coal; ○ 1 A/dm<sup>2</sup>; ■ 2 A/dm<sup>2</sup>; □ 4 A/dm<sup>2</sup>

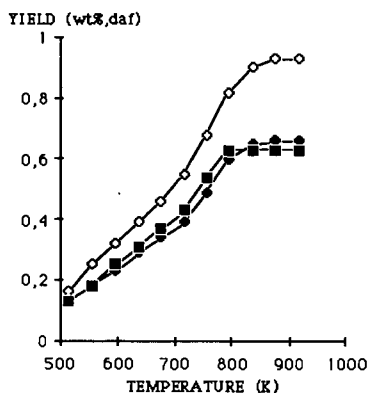


Fig. 3 Effect of Cell Type in ER Pretreatment on CO<sub>2</sub> yield in HyPy under 3 MPa, 5 K/min. ER: 40% TBAOH, 4 A/dm<sup>2</sup>, 60 °C, 0.022 F/g(daf). ● Raw Coal; ○ ER-Undiv. Cell; ■ ER-Divided Cell.

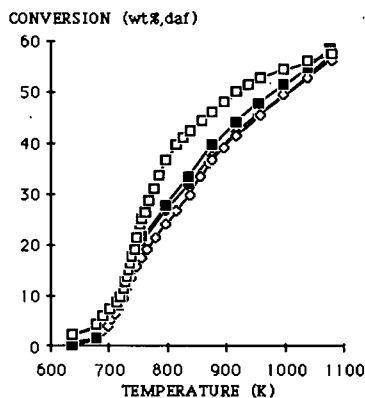


Fig. 4 Effect of ER Pretreatment on Conversion under 3 MPa, 5 K/min. ER: TBABF<sub>4</sub>-THF-H<sub>2</sub>O, 33 °C, 0.6 A/dm<sup>2</sup>, 0.022 F/g(daf). ● Raw Coal; ○ Solvated; ■ ER-Undiv. Cell; □ ER-Divided Cell.

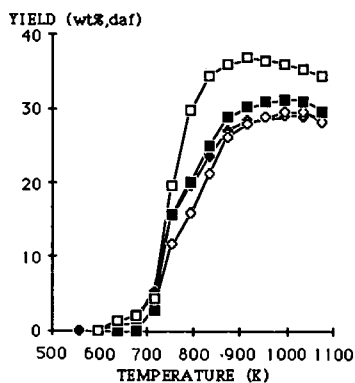


Fig. 5 Effect of ER Pretreatment on Oil Yield in HyPy under 3 MPa, 5 K/min. ER: 0.6 A/dm<sup>2</sup>, TBABF<sub>4</sub>-THF-H<sub>2</sub>O, 33 °C, 0.022 F/g(daf). ● Raw Coal; ○ Solvated; ■ ER-Undiv. Cell; □ ER-Divided Cell.

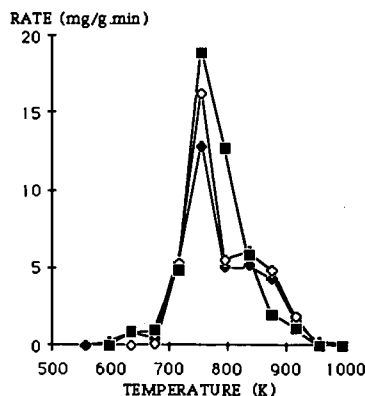


Fig. 6 Effect of ER Pretreatment on Rate of Oil Formation in HyPy under 3 MPa, 5 K/min. ER: TBABF<sub>4</sub>-THF-H<sub>2</sub>O, 0.6 A/dm<sup>2</sup>, 33 °C, 0.022 F/g(daf). ● Raw Coal; ○ ER-Undiv. Cell; ■ ER-Divided Cell.